

Electromagnetic theory of surface-enhanced Raman scattering

N. N. Gorobeĭ, I. P. Ipatova, and A. V. Subashiev

A. F. Ioffe Physicotechnical Institute, Academy of Sciences of the USSR, Leningrad

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A macroscopic theory is derived for surface-enhanced Raman scattering. The enhancement can be explained by the field intensification which occurs near a point at which the dielectric constant vanishes.

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Experiments on the Raman scattering by molecules adsorbed on the surfaces of various metals have shown that the scattering cross section in this situation is five or six orders of magnitude larger than that of the same molecules in a pure medium.^{1,2} In this letter we will show that this surface-enhanced Raman scattering (or “giant intensification” of Raman scattering) can be explained by the well-known field intensification^{3,4} which occurs near a point at which the dielectric constant vanishes as electromagnetic waves propagate through an inhomogeneous medium. An analogous scattering enhancement was predicted by Piliya⁵ and has recently been observed in an inhomogeneous plasma by Budnikov *et al.*⁶

According to Rowe *et al.*⁷ the characteristic dimensions of the surface relief (200–2000 Å) are much smaller than the wavelength of visible scattered light. We may thus introduce the concept of a transitional surface layer in which the effective dielectric constant $\epsilon(z)$ varies along the coordinate z , which runs perpendicular to the surface of the metal, but is constant along the Ox and Oy axes. The thickness of this layer, d , is smaller than the skin depth and much smaller than the wavelength of the light. Within this transition layer, ϵ changes from its value of $\epsilon = 1$ in a vacuum to a large negative value ϵ_m in the metal. The profile $\epsilon(z)$ thus has a point at which $\epsilon = 0$. Near this point, the $\epsilon(z)$ dependence can be assumed linear. We thus have a model of a multilayer vacuum–(linear layer)–metal structure for this system.

Let us consider the case of the oblique incidence of a light wave $\mathbf{E}^I = (E_x^I, 0, E_z^I)$ which is polarized in the plane of incidence, in accordance with the experiments of Ref. 7. The most convenient approach for solving the light-scattering problem is to calculate the field of the scattered wave from Maxwell's equations, in which ϵ has a small increment $\delta\epsilon_{\mu\nu}(t)$ which fluctuates because of intramolecular vibrations of the adsorbed molecules. For simplicity, we shall consider scalar scattering by a single, completely symmetric vibration of the l th molecule in the linear layer at the point $\mathbf{r}_l = (0, 0, Z_l)$, for which $\delta\epsilon_{\mu\nu} = \delta_{\mu\nu}\delta\epsilon$. The total dielectric constant of the transition layer is

$$\epsilon(z, t) = az + \delta\epsilon(t), \quad \delta\epsilon \doteq \alpha_0 \delta(\mathbf{r} - \mathbf{r}_l) e^{-i\Omega t}, \quad (1)$$

where a^{-1} is a parameter of the order of d , the thickness of the transition layer;

$a_0 = v_0 \partial \epsilon / \partial Q Q_0$, (v_0 is the volume of a molecule), and Ω and Q are the frequency and normal coordinate, respectively, of the active vibrational mode of the l th molecule.

The field of the scattered wave, \mathbf{E}^S , can be found by the usual method of successive approximations in the small parameter $E^S/E^I \ll 1$. The wave equation determining the field $\mathbf{E} = \mathbf{E}^I + \mathbf{E}^S$ in the linear layer is

$$\nabla \times \nabla \times \mathbf{E} - a z \frac{\partial^2 \mathbf{R}}{\partial t^2} = (k^I)^2 \delta \epsilon \mathbf{E}^I, \quad (2)$$

where k^I is the wave number of the incident light wave.

The field of the incident wave inside the layer, \mathbf{E}^I , is also determined from Eq. (2), with $\delta \epsilon = 0$ and with boundary conditions which depend on the particular model adopted for the transition layer. We assume here that ϵ varies in accordance with linear law (1) over the interval $-d/2 < z < d/2$ in the layer and jumps discontinuously at $z = -d/2$ to the value $\epsilon = \epsilon_m$. The results of the calculation actually depend on the parameter a in (1) and are relatively insensitive to the details of the $\epsilon(z)$ behavior. In the lowest-order approximation in the small parameter $k^I d \ll 1$, and under the assumption that $|\epsilon_m| \gg 1$, we find

$$E_x^I = E_0^I \left\{ ik^I d [\sin^2 \theta_i \ln |2z/d| - 2z/d] - \frac{2 \cos \theta_t}{\sqrt{\epsilon_m}} \right\}, \quad (3)$$

$$E_z^I = E_0^I d \sin \theta_i / z; \quad \sin \theta_i = \frac{k_x^I}{k^I}, \quad \sin \theta_t = \frac{k_x^I}{k^I \sqrt{\epsilon_m}},$$

where E_0^I is the amplitude of the incident wave, and k_x^I is the x component of the wave vector k^I . In the zeroth approximation in $k^I d \ll 1$, the coefficients of the reflected wave (in the vacuum) and of the refracted wave (in the metal) are the same as those given by the Fresnel equations.

To find the field of the scattered wave \mathbf{E}^S produced by a molecule at the point z_l , we seek a solution of Eq. (2) as a Fourier expansion in the polar coordinate system (k_\perp^S, ϕ_k) in the first approximation in the fluctuating increment $\delta \epsilon$, where $(k_\perp^S)^2 = (k_x^I + q_x)^2 + (q_y)^2$, q_x and q_y are the components of the momentum transferred by the molecule as a result of the scattering, and $\tan \phi_k = q_y / (q_x + k_x^I)$.

The solution of Eq. (2) can be expressed in the standard way in terms of its Green's function,⁸

$$E_{ki}^S = \alpha_0 (k^I)^2 \int D_{ij}(z, \zeta; k_\perp^S) E_j^I(\xi) \delta(z_l - \zeta) d\xi, \quad (4)$$

where $D_{ij}(z, \zeta; k_\perp^S)$ are the components of the Green's function, and $i, j = x, y, z$.

It is important to note that the component D_{zz} has a singularity at small values of z , and it is this singularity which determines the enhancement of the emission by a

source near the $z=0$ plane. After determining the Green's function, using the boundary conditions at $z=\pm d/2$ and the condition $k^S d \ll 1$, we find the field of the scattered wave to be $\mathbf{E}_k^S = \mathbf{E}_{k_0}^S e^{ik_{\parallel}^S z}$, where

$$\mathbf{E}_{k_0}^S = E_0^I \frac{\alpha_0 (k^I)^2}{i k^S} \left(\frac{d}{2z_l} \right)^2 \Phi \left[\mathbf{e}_x + \frac{k_{\perp}^S}{k_{\parallel}^S} \mathbf{e}_z \right]. \quad (5)$$

Here $(k_{\parallel}^S)^2 = (k^S)^2 - (k_{\perp}^S)^2$; \mathbf{e}_x and \mathbf{e}_z are unit vectors along the Ox and Oz axes; and the quantity Φ , a function of the angles, is defined by

$$\Phi = 2 \sin \theta_i \sin \theta_i^S, \quad \sin \theta_i^S = \frac{k_{\perp}^S}{k^S}. \quad (6)$$

Taking the inverse Fourier transform of the field \mathbf{E}_k^S , and expanding the plane wave $e^{ik^S r}$ in spherical harmonics, we find the field \mathbf{E}^S at an observation point at a large distance r from the scattering molecule:

$$\mathbf{E}^S(\mathbf{r}, t) = \mathbf{E}_{k_0}^S (\cos \theta) \frac{k^S}{r} \cos \theta e^{ik^S r}, \quad (7)$$

where θ is the azimuthal angle of the observation point.

It follows from (5) that the scattering is dominated by molecules in the strong-field region. If d is not too small, the size of this strong-field region and the strength of the field are determined by absorption, i.e., by $\text{Im} \epsilon$.

Let us assume that $\text{Im} \epsilon$, like $\text{Re}(\epsilon - 1)$, is proportional to the average electron concentration in the layer, which varies along z . Near $z=0$ we then have $\text{Im} \epsilon(0) = \text{Im} \epsilon_m / \text{Re} \epsilon_m$. We accordingly replace az in (2) by $az + i \text{Im} \epsilon(0)$. (The absorption is negligible far from the point $z=0$.) Taking an average over the positions of the molecules along the oz axis (integrating the intensity over z_l within the layer), we find the time average of the intensity of the light scattered into a solid-angle element $d\tilde{\Omega}$ to be

$$\overline{dI} = \frac{c}{16\pi^2} \alpha_0^2 (k^I)^4 (\Phi E_0^I)^2 \left(\frac{\text{Re} \epsilon_m}{\text{Im} \epsilon_m} \right)^3 d\tilde{\Omega}. \quad (8)$$

Expression (8) contains the factor $G = (\text{Re} \epsilon_m / \text{Im} \epsilon_m)^3$, which is not found in the expression for the intensity of the light scattered by a molecule in a pure medium. This new factor describes the enhancement of the scattering at the rough metal substrate. Estimates based on the optical constants of copper, silver, and gold for various wavelengths show⁹ that G is highest in the case of silver, which has the lowest value of $\text{Im} \epsilon_m$ in the optical wavelength range. An order-of-magnitude estimate for silver yields $G = 5 \times 10^4$ for $\hbar\omega^I = 2.1$ eV (ω^I is the frequency of the incident light), in accordance with the experiments of Ref. 7. The factor G increases with decreasing $\hbar\omega^I$ and reaches a maximum $G = 10^6$ at $\hbar\omega^I = 1.14$ eV. The region of the maximum field, which is limited by absorption, has a thickness $d/G^{1/3}$ and becomes smaller as d decreases. The minimum size of the strong-field region is of the order of the dimensions of the molecule, r_0 , so that the maximum field for a small thickness d is

$E^S \sim E_0^I (d/r_0)^2$. The coefficient G , therefore, is no greater than $(d/r_0)^3$ in any case, and it vanishes in the case of a smooth surface. The factor Φ^2 in (8) describes the strong angular dependence of the scattering, in particular, there is no scattering along the direction perpendicular to the surface.

Chen *et al.*¹⁰ have recently observed a pronounced increase in second-harmonic generation upon reflection from the rough surface of a pure metal; this observation is direct evidence of a pronounced intensification of the field near the metal surface.

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